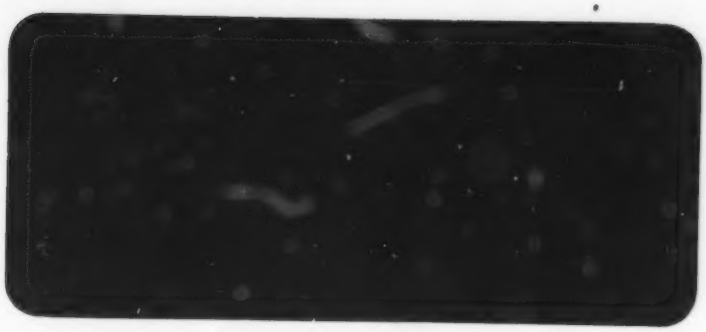

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CONTRACT SERIAL NO. 23440-09278-01-SQ

CONTRACTOR: ATLANTIS SCIENTIFIC

CARS PROJECT REPORT FOR EMR
REQUISITION # 23440-0-9278
24 MARCH 1992

MICROMEDIA

20 pp

# Coherent Anti-Stokes Raman Spectroscopy (CARS) Project Report for EMR - CARS Spectra of Nitric oxide (NO) and Other Software Developments

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24 March 1992

[1]supported by requisition number 23440-0-9278 from EMR

92-06768/

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# 1 Introduction

The continuous development of a specialized software package for generating the theoretical spectra and for analyzing the experimental spectra collected from Coherent Anti-Stokes Raman Spectrocopy, (CARS) has been sponsored by Energy Mines and Resources (EMR), the National Research Council (NRC) and the Defence Research Establishment Val Cartier (DREV). Information on the CARS technique and the capabilities of the existing CARS software can be found in previous reports (Parameswaran, 1991a, Parameswaran and Snelling 1988) and the references therein.

The original CARS software was developed by T.Parameswaran and D. Friend of Atlantis Scientific, in a DEC VAX-11 computer using the fortran language. During 1991, under collaborative support from EMR and NRC, the VAX versions of the software were transported to a personal computer (PC) environment. These versions existing in 386 or 486 based PC's were modified to work with NDP fortran supported by Microway Systems. In this conversion process several subroutines had to be modified, some VAX system dependent routines had to be replaced and additional subroutines had to be written. Under the DOS environment file names do not have version numbers. Special code was written to have the file names defined as `FILENAME.Xnn` in the CARS programs such that the character X can be used to identify a file type and nn was chosen to lie between 01 and 99 and thus serve as an artificial version number. The CARS plotting programs in the VAX employ Tektronix PLOT-10 software. In the PC versions these were substituted with the INGRAF library from Sutrasoft systems. This conversion of the program `PLT_PROGRAM` was mostly done by G. Bernard of NRC. The new programs were compiled and linked with NDP fortran version 3.2 and Pharlap tools version 4.0. The software also requires a Weitek or Intel 80387 math coprocessor and additional random access memory of 16 megabytes. A more detailed account of all the features of the PC versions can be found in the updated 1992 versions of the User Manuals for the CARS software package.

The current report describes the various tasks performed by the author to upgrade the PC versions of the CARS software to detect the presence of nitric oxide ($NO$) in flames and to address several other concerns associated with the CARS spectral analysis. This work was made possible by a contract from EMR.

# 2 The nitric oxide molecule (NO)

## 2.1 Energy level structure of $NO$

Nitric oxide is a diatomic molecule with a complex energy level structure. The complexity arises because it has an electronic ground state $\pi^2$ which is a doublet with an orbital angular momentum L=1 and a spin S= 1/2. The electronic orbital angular

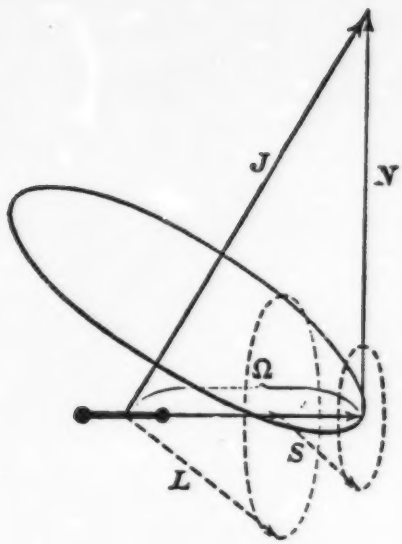


Figure 1: Vector Diagram for Hund's case (a) as in NO

momentum comes from the presence of an unpaired electron. In a molecule the electronic orbital angular momentum **L**, the electron spin **S** and the angular momentum of nuclear rotation **N** combine to form the total angular momentum **J**. If **L** and **S** are zero then the molecule has a $\Sigma^1$ state and **J** equals **N**. This is typically the case for molecules such as $N_2, CO, H_2$ etc. When this is not true the resultant level structure and spectra depend on the relative coupling betwen **L**, **S** and **N** as indicated by Hund's rules. In Hund's case(a) it is assumed that the coupling of electronic orbital and spin angular momenta with nuclear motion is weak but the electronic motion is very strongly coupled to the internuclear axis. Thus **L** and **S** first couple to form a resultant vector $\mathbf{\Omega}$ which then combines with **N** to form the total **J** as shown Figure.1 (Herzberg 1963). In this figure $\mathbf{\Omega}$ and **N** nutate about **J** while **L** and **S** precess about the internuclear axis. In NO, $\mathbf{L} = 1$ with the component of orbital angular momentum along the inter nuclear axis $M_L = \pm 1$ and component of spin angular momentum along the inter nuclear axis $M_S = \pm 1/2$. The total electronic angular momentum $\mathbf{\Omega}$ can have values 1/2 or 3/2 giving rise to two states split by spin orbit interaction by about 124 $cm^{-1}$. These electronic angular momenta further combine with the nuclear rotation to give the total angular momentum **J** of the molecule for each state. The double degeneracy of these states due to the $\pm$ values of $M_L$ is often referred to as $\Lambda$ doubling. In Hund's case (a) the coupling between electronic motion and nuclear rotation is neglected. As the speed of rotation increases with **J**, this coupling comes into effect and causes a small splitting ( fraction of a $cm^{-1}$) of the above doublets. Thus in $NO$ there are two closely spaced ground state levels each giving rise to its own vibration rotation or Q branch spectrum. The lower $\Omega = 1/2$ state has an oscillator frequency of 1876.089 $cm^{-1}$ and the $\Omega = 3/2$ state has an oscillator

frequency of 1875.881 $cm^{-1}$.

## 2.2 The theoretical CARS spectra of *NO*

The theoretical CARS spectrum of a molecular species in a combustion environment is obtained by calculating the third order nonlinear electric susceptibility, by properly summing the contributions from the various rovibrational transitions. In the case of *NO* both the Q branches from the split ground state have to be taken into account in this theoretical modelling.

The program SPT_GENERATE and the subroutines it calls, were modified to make a preliminary calculation of the theoretical CARS spectrum of NO. Specifically, several subroutines in the library THRYLIB needed to be modified to accommodate the NO molecule. For these initial calculations the molecular constants from Herzberg (Herzberg, 1979) were used.

They are:

for the $\Omega = 3/2$ branch,

- $\omega_e = 1904.04$
- $x\omega_e = 14.100$
- $y\omega_e = 0.011$
- $z\omega_e = 0.0$
- $B_e = 1.72016$
- $D_e = 10.2 \times 10^{-6}$
- $\alpha_e = 0.0182$
- $\gamma e = 0.0$
- $\beta_e = 0.0$

and for the $\Omega = 1/2$ branch

- $\omega_{e1} = 1904.20$
- $x\omega_{e1} = 14.075$
- $y\omega_{e1} = 0.007$
- $z\omega_{e1} = 0.0$

- $B_{e1} = 1.67195$
- $D_{e1} = 0.5 \times 10^{-6}$
- $\alpha_{e1} = 0.0171$
- $\gamma_{e1} = 0.0$
- $\beta_{e1} = 0.0$

The non resonant susceptibility of 25.3 $\times 10^{-18} cm^3/erg$ was obtained from the work by Lundeen et al.(1983). The rotational relaxation matrix elements and the Raman linewidths were computed according to the scaling law suggested by Lempert et al. (1984). Then the rate $\gamma$ for energetically downward transitions is given by

$$\gamma_{J \leftarrow J'}^{\Omega \leftarrow \Omega} = A_\Omega \frac{(2J_< + 1)}{(2J_> + 1)} (\Delta E / B_0)^{-\beta} exp(-C\Delta E / KT) \qquad (1)$$

where $J_<$ is the lesser of $J$ and $J'$, $\Delta E$ is the absolute value of the energy diffeence between the two levels, $A_{3/2} = 0.0144 cm^{-1}$, $\beta = 0.2, C = 0.3$, $B_0 = 1.7 cm^{-1}$ and $X = A_{3/2}/A_{1/2} = 1.6$

In the present calculations only the relaxation between states within each Q branch was considered. The linewidths FWHM thus calculated for the states J=3/2 to J=27/2 do not quite agree with the values in Lempert etal.'s paper. The present values lie between 0.11 and .09 for the $\Omega = 3/2$ branch and .072 and 0.058 for the $\Omega = 1/2$ branch. The experimental values given in Lemper etal.'s paper range between 0.075 and 0.063 for the $\Omega = 3/2$ branch and 0.064 and 0.054 for the $\Omega = 1/2$ branch. This may be the result of neglecting the interelectronic transitions in the linewidth calculation and(or) because more accurate calculation of the molecular frequencies are required.

The Raman cross section was held fixed and the value 2.02 $\times 10^{-48} cm^6/sr$ the average value from the data compiled by Schrotter and Klockner (1979). The 1/2 and 3/2 Q branches were considered and summed in calculating the CARS field amplitude. Overlap of transitions with different $\Omega$ was neglected for simplicity.

Inorder to see the doublet structure in the CARS spectrum of NO the pump convolution had to be performed with a very narrow bandwidth of ¡ 0.005 $cm^{-1}$. Larger pump bandwidths wash out the doublet splitting. Room temperature pure NO spectrum calculated in the region 1874-1877 $cm^{-1}$ region with a pressure of 0.17 atm. is shown in Figure 2. This is a pump convolved spectrum and no slit convolution was performed. It appears to have a shape very similar to that of the Q branch spectrum of NO obtained by Lempert et al.(1984) shown in Figure 3. This spectrum was generated by stimulated Raman spectroscopy at a pressure of 0.17 atm. and at a temperature of 298 K. The two Q branches are clearly seen in both the figures. In the

absence of experimental data or other calculated results this was the only comparison that could be made at the time.

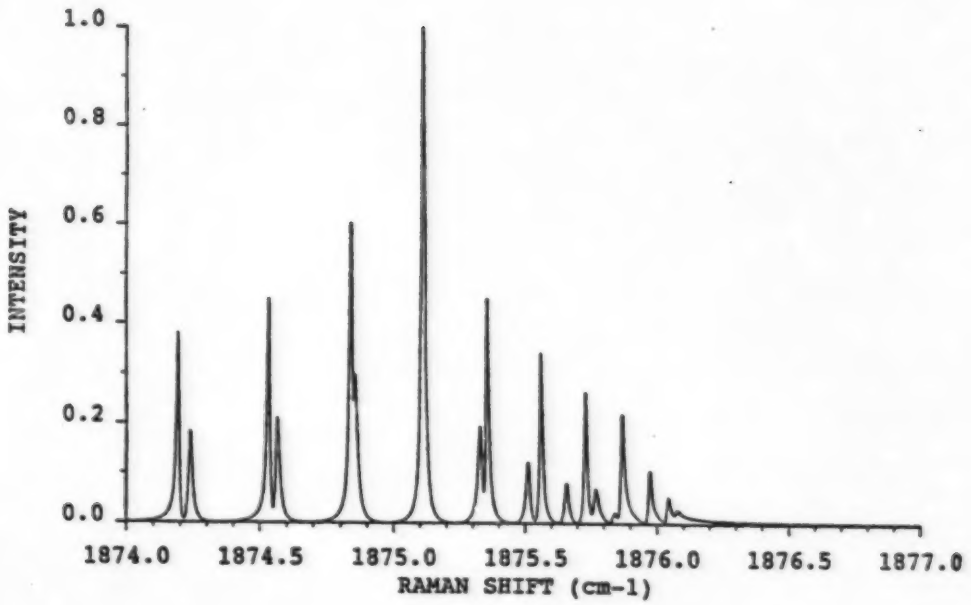


Figure 2: The theoretical CARS spectrum of nitric oxide

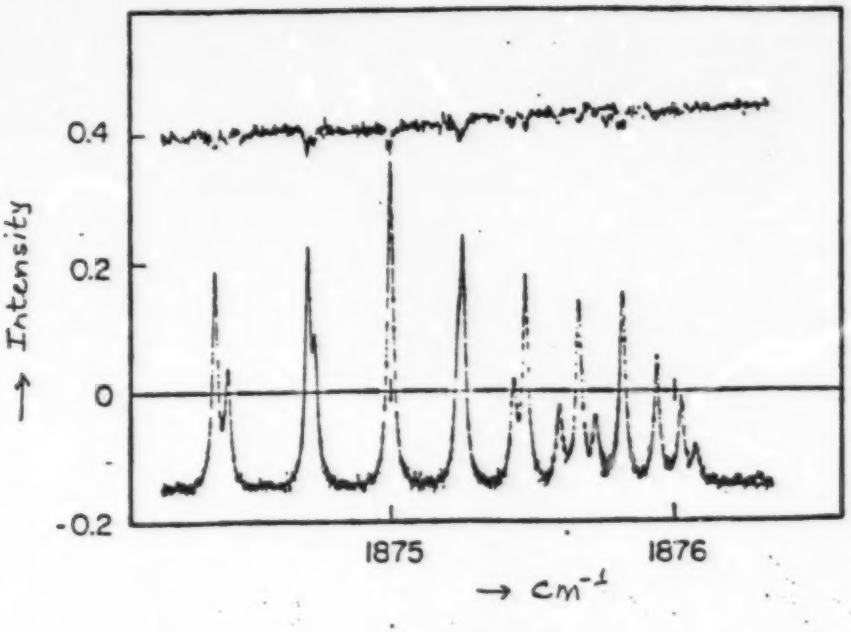


Figure 3: Q branch spectrum of nitric oxide from Lempert et. al's work)

## 2.3 Input data file for NO

A complete input data file required for the CARS spectrum calculation of NO with the program SPT_GENERATE is given below.

```
$MOL
MOLECULE_NAME = 'NO'
$END
$MODL
MODEL =  'GT'
GDIAG =  'ALL'
SCLNG  =  'SN '
ADNL_BRD_CORR  = 0.0
CROSSCTN_PRM = 1
NARR_COEF    = 0.
PHASE    = 0.
$END
$RUNVAR1
PRESSURE          =  0.1700000
MOLE_FRAC         =  1.000000
NON_RESN_SUSCEP   =  25.3E-18
START_TEMP        =  298.0E+00
FINISH_TEMP       =  298.0E+00
TEMP_STEP         =  500.0E+00
$END
```

```
$RUNVAR2
PUMP_WID          =  0.005
PUMP_CENTR_FREQ   =  18797.
NUM_THTCL_PARTS     = 1
SPEC_TYPE      ='PUMP_CONV'
FILE_TYPE      ='SPT'
CWRITE         = 'PARTIAL'
CONST1         = 1.
CONST2         = 0.
$END
$FRQ
CHI_SQR_GRID     =  0.0003
PUMP_CONV_GRID   =  0.003
STRT_FREQ        =   1874.00
FIN_FREQ         =   1877.00
FIRST_WN_SLIT = 1874.1
LAST_WN_SLIT  = 1876.9
FIRST_WN_FIT  = 1874.2
LAST_WN_FIT   = 1876.8
TRAN_MIN = 0.,
FAST_VERSION  = 'N'
CRSE_GRID      = 0.04
$END
$SIGMA
RAM_SIGMA  = 2.02E-30
$END
$MEGLAW
ALPHAT0 =0.0144
BETA = 0.2
DELTA = 0.3
T0 = 0.7
POWER = 0.005
MVAL = 1.6
APARAM = 1.7
YOFF = 0.
$END
$MOLCONS
WE       =   1904.04
XWE      =   14.100
YWE      =   0.011
ZWE      =   0.0
BE       =   1.72016
```

```
DE       =  10.2E-06
ALPHE    =  0.0182
GAME     =  0.0
BETE     =  0.0
DELTE    =  0.
H0       =  0.0
HE       =  0.0
C4       =  0.
C5       =  0.
NUC_STAT=  1.000000     ,    1.000000
$END
$MOLNO
WE1    =    1904.20
XWE1     =    14.075
YWE1   =    0.007
ZWE1       =    0.0
BE1    =    1.67195
DE1    =    0.5E-06
ALPHE1     =    0.0171
$END
```

In this input data file, the molecular constants for the $\Omega = 3/2$ state are given under the namelist MOLCONS and those for the state $\Omega = 1/2$ are given under the namelist MOLNO. Also the parameters for the hybrid exponential gap scaling law (Lempert et al. 1984) used for *NO* are renamed as follows: A = ALPHAT0 ; BETA=BETA; C = DELTA; S = T0; $k_0$ = POWER; X = MVAL; B0 = APARAM. Since interelectronic transitions have been neglected the parameters S and $k_0$ were not used in computing the linewidths.

These are only preliminary calculations. In future work contributions from pure spin flip and other interelectronic transitions where spin and rotational angular momenta change, will also be included. Further, more accurate estimates of the line positions using the molecular constants of Valentin et al.(1978) will be done. The effect of the overlap of transitions in the two Q branches will be explored. When experimental spectra become available comparisons between theory and experiment will be made at different conditions of temperature, pressure and NO concentrations.

# 3 Average spectra in turbulent flames

In a laboratory flat flame the temperature at a point does not vary very much so that the average of several CARS spectra collected will not differ greatly from the individual spectra. In turbulent flames that occur in practical applications, this is

not true. CARS spectra collected over a period of time, within the focal volume, can have a large spread in temperature and concentrations. In this case a straight average of the spectra collected may not represent a true spectrum. In CARS analysis it is often necessary to compare the best fit temperature obtained for the average spectrum with the average of the best fit temperatures of the individual spectra. To do this comparison a meaningful average spectrum is needed. The program SPT_AVERAGE was written to fulfill this requirement.

Experimental CARS spectra are stored in binary files with fixed length, structured records. Such files have the extension .SPT in the DEC VAX-11 computer and .Snn in the PC computers. In the latter case nn can range from 01 to 99 and these numbers are used to identify the file version. The program SPT_AVERAGE reads spectra from such an experimental file and sorts them according to temperature or integrated intensity. These ordered spectra are then separated into subgroups and placed into smaller files along with their respective average. These new files are structured similar to the original file and can be analyzed or plotted in the same way. However each of these subfiles contain a set of spectra with temperatures within a small range and hence their average is more meaningful. If the original file has already been analyzed with the program SPT_FIT the resulting temperatures can be used for ordering the spectra. When this is not the case the intensity bin option can be selected. This will make SPT_AVERAGE calculate the integrated intensity of each spectrum within a user prescribed range and use these intensities for ordering and grouping the spectra. The number of spectra in each group or bin is user selected. Examples of the use of SPT_AVERAGE are given in the user manual for that program.

# 4 Dye laser centre frequency as a fit parameter

In a CARS experiment the centre frequency of the dye or Stokes laser plays an important role. During an experiment this frequency may drift by several diodes due to variation in the temperature, concentration or other reasons. To be able to properly fit the CARS spectra it is desirable to quantify the effect of this shift of the dye centre frequency on the CARS temperartures. At the outset it would seem that we can add this shift as another parameter that may be determined by the fitting program that performs the CARS data analysis. This may be achieved by the following steps.

1. The nonresonant CARS spectrum basically provides the shape of the dye laser profile. Fit the nonresonant CARS spectrum to an appropriate function f(i) which may be a Gaussian. The index i in this and other functions below is the diode number of the detector.
2. Divide the nonresonant spectrum by this Gaussian function to obtain the diode to diode sensitivity curve f'(i). Divide the resonant CARS spectrum by f'(i).

3. Shift the Gaussian by a trial amount and multiply it with the trial theoretical function. This function will provide the trial theoretical spectrum for subsequent analysis of resonant CARS spectra.
4. Repeat step 3 in each iteration and get the best fitting value for the dye laser shift along with the other fit parameters.

The above procedure seems quite good and can be implemented. However, we must recall that a relative frequency shift between the experimental CARS spectrum and the theoretical spectrum is aleady a parameter in the current fitting scheme. This shift allows a translation of the experimental CARS spectrum along the frequency axis after it is divided by the nonresonant spectrum. The nonresonant spectrum is essentially the profile of the Stokes laser. If we now include the shift of the dye centre frequency or the nonresonant spectrum as an additional parameter which is simultanously varied along with the relative shift mentioned earlier and the other fit parameters, it is quite likely that there will be an interaction between the two shifts and it may cause convergence problems.

Therefore an alternative method for estimating the effect of the dye laser drift on the CARS spectra was implemented in the existing program `SPT_FIT` which performs the data analysis. The program now has the option of performing a given analysis with a shifted nonresonant spectrum. This is done as follows:

1. Read a shift parameter `DYE_SHIFT` from the FITDATA file. If this parameter is zero the nonresonant spectrum is left as is. If `DYE_SHIFT` is nonzero, do the following steps to shift the nonresonant spectrum.
2. Read a spectrum u(i) corresponding to the uniform illumination of the diode array, from a separate file.
3. Divide the nonresonant spectrum f(i) by the spectrum u(i) to get f'(i).
4. Shift f'(i) by the desired value `DYE_SHIFT` in diodes, and then multiply with u(i) to give f"(i).
5. Save the original f(i) and the shifted f"(i) nonresonant spectra in a text file `NR_SPEC.LIS`.
6. Use f"(i) as the shifted nonresonant spectrum used for dividing the resonant CARS spectrum.
7. Fit parameters obtained with and without shifts of the nonresonant spectrum can be compared to see the effect of dye laser drift. Since `DYE_SHIFT` stays constant during a fit it will not interact with the relative shift between experiment and theory used in the standard fitting scheme.

## 4.1 Effect of dye laser shift on CARS temperatures

To understand the systematic error in the CARS derived temperatures that might be caused by a change in the centre frequency of the dye laser the following study was done. A CARS data file with 800 spectra generated at NRC was analyzed with and without a shift of the nonresonant spectrum. For these test calculations the spectrum of uniform illumination of the diode array was chosen to be a flat spectrum with equal intensity at all diodes. The shift in the CARS best temperature is plotted against the temperature in figures 4 and 5. Figure 4 corresponds to a positive shift of 10 diodes while figure 5 was obtained with an equal but negative shift. These data suggest that the shift in temperature increases with temperature and the percentage shift lies in the range 1.0 to 3.0. Results obtained in this study are not unique and should be associated with the specific experimental setup used. In this case the rhodamine dye laser used had a bandwidth of about 70 $cm^{-1}$ and the peak of the dye laser was arranged to coincide with the 3-2 band of nitrogen.

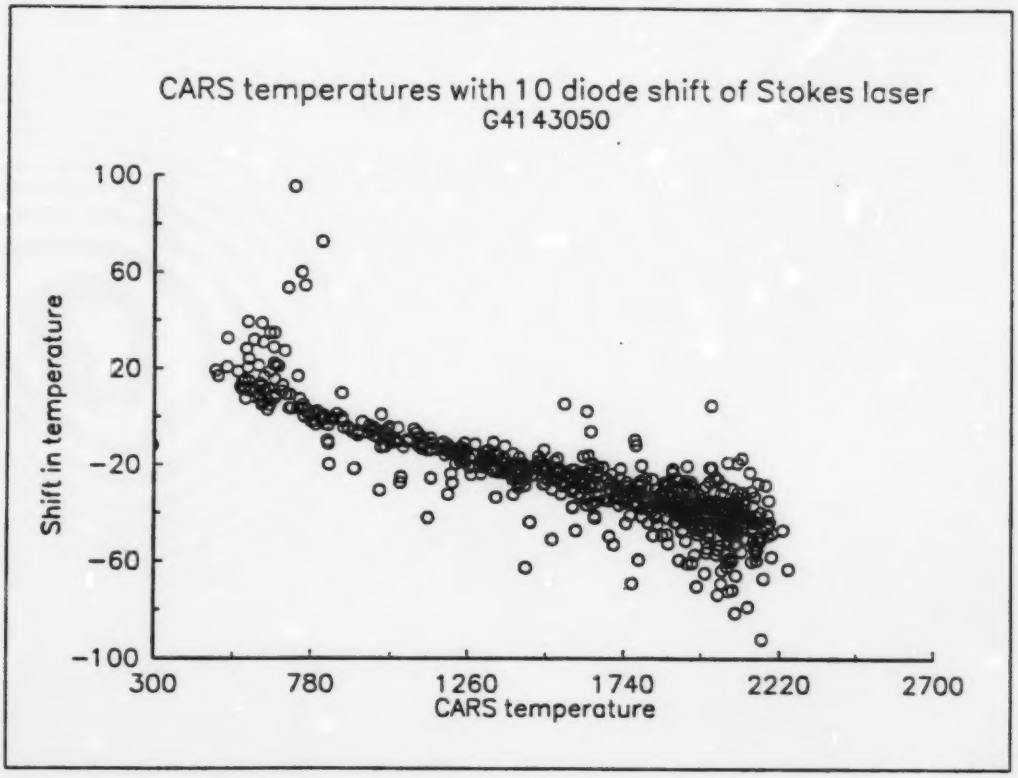


**Figure 4: Shift in CARS temperatures with a dye shift of plus 10 diodes**

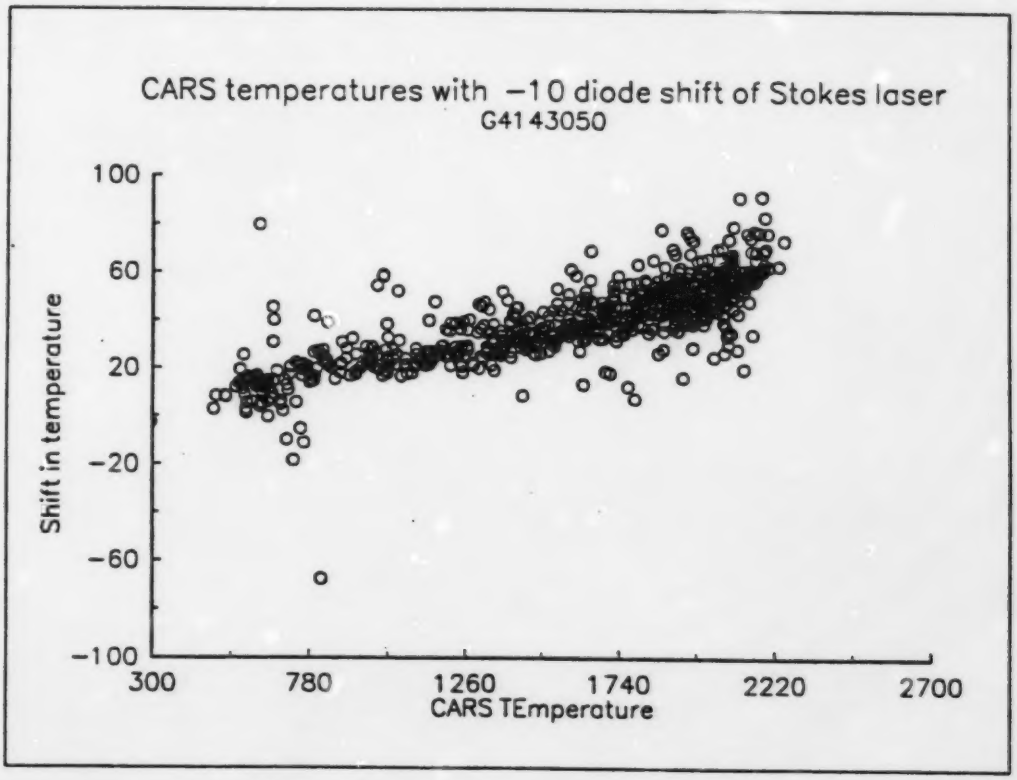


**Figure 5: Shift in CARS temperatures with a dye shift of minus 10 diodes**

# 5 Features added to the fitting program

SPT_FIT is a versatile fitting program. Recent developments in the analysis of CARS spectra at NRC and EMR have necessitated the addition of further capabilities to this program. These modifications are summarized below.

1. When a CARS spectral file is analyzed the best fit temperature is calculated for each spectrum and a straight average of the temperatures for the entire file is also calculated. In combustion diagnostics it is often desirable to know not only this simple average $T_s$ but also the density weighted average $T_d$ and the density square weighted average $T_{d^2}$. Since density is inversely proportional to the temperature T, $T_d$ is obtained by using T as the weight and $T_{d^2}$ is obtained with $T^2$ as the weight. Therefore the program SPT_FIT was modified to compute

$$T_d = \frac{Number of spectra}{\Sigma_i(1/T_i)} \tag{2}$$

$$T_{d^2} = \frac{\Sigma_i(1/T_i)}{\Sigma_i(1/T_i^2)} \tag{3}$$

where i is the spectrum index.

In addition the average radiation temperature defined by

$$T_{rd} = \frac{\Sigma_i(T_{i^4})}{Number of spectra} \tag{4}$$

was also calculated and these values were saved in the summary file.

2. The integrated intensity of the experimental spectra and the undispersed intensities of each spectrum were included in the list of variables saved in the "T" file. The spectra that did not converge at the end of the maximum number of cycles were excluded from the "T" file.

3. When temperature and concentration are fitted simultaneously with a data set of turbulent spectra, it is often difficult to choose good initial guesses. If these are too far from the final values, convergence can be difficult and slow. Therefore additional code was implemented in the fitting program to first make a quick estimate of the variances of the average spectrum for a coarse set of temperature and concentration and select the values corresponding to the minimum variance as the initial guesses for the individual spectra. This approach was found to be very useful with files containing spectra of widely varying temperatures. This quick method is used only when the slit function is not fitted at the same time.

4. Constraints were introduced so that the temperatures were forced to stay within the theoretical library range and concentrations to be greater than 0.1 and less than the value for pure nitrogen. Care had to be taken to ensure that these constraints are obeyed even during the estimation of differentials for the Gauss Newton least mean square fit.

5. In initial CARS analysis an asymmetric Voigt function was used used to represent the instrumental slit function. More recently it was realized that a symmetric Voigt function would be more appropriate and hence the fitting program was modified where nececessary to handle this change.

# 6 Other tasks

Some of the additions and improvements described above were first included in the VAX versions of the programs and then transported to the PC environment while others were introduced directly into the PC versions. It was ascertained that the VAX computer at EMR had all the latest versions of the CARS programs as maintained at NRC.

Under earlier contracts User manuals were written for the VAX versions of the CARS programs. These manuals were updated to reflect the recently implemented modifications and the transfer to the PC environment.

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